

Electronic Supplementary Information (ESI)

A fluoropolymer bifunctional solid membrane interface for improved discharge duration in aqueous Al-air battery

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Experimental

Preparation of aqueous Al-air battery

In the current study, aqueous Al-air battery are composed of the anode, cathode and electrolyte. The preparation of battery is as follows:

(1) Commercial Al alloy Al-1060 plate (Shenzhen Shengjili Co., Ltd) with a purity of 99.6% was selected as the pure Al anode. In a vacuum glove box, specific amount of 60% DISP-30 Fluoropolymer Dispersion (The Fuel Cell Store) was dissolved in isopropanol (IPA, Shanghai Meryer Co., Ltd). Considering the factors of the anticorrosion effect, charge transfer impedance and cost, the 5% polytetrafluoroethylene (PTFE) solution was obtained firstly. And then, the solution was stirred for 1 h and ultrasonically oscillated for 2 h. After polishing, Al-1060 plate was soaked in the solution for 6 h, and continuously heated at 80 °C in the oven for 12 h after taking out. Finally, an Al anode with PTFE solid membrane interface (SMI) was prepared.

(2) 50 mg $C_4H_7FeO_5$ (Shanghai Acme Biochemical Co., Ltd), 85 mg $Co(NO_3)_2 \cdot 6H_2O$ (Shanghai Meryer Co., Ltd), 55 mg MnO_2 (Shanghai Meryer Co., Ltd), 25 mg CH_4N_2S (Shanghai Acme Biochemical Co., Ltd) and 40 mg porous carbon nanotubes (Suzhou Hengqiu Technology Co., Ltd) were dissolved in 1 mL 60% IPA. After the mixture was heated in a water bath at 70 °C for 1 h, it was put into a high-temperature tube furnace and heated at 220 °C for 2 h to obtain oxygen reduction reaction (ORR) catalyst powder. The powder was mixed with Nafion solution (Suzhou Sinero Technology Co., Ltd) and sprayed onto the surface of carbon paper attached to the nickel foam to prepare an ORR air cathode.

(3) A specific mass of KOH (Tianjin Damao Chemical Reagent Co., Ltd) was put into deionized water (Shanghai Tian Scientific Co., Ltd) to form the 0.1 M KOH electrolyte, which was used in the current study.

The above components were assembled together to manufacture the aqueous Al-air batteries using Al anodes with and without PTFE SMI.

Al anode self-corrosion test

At the atmosphere of 25 °C and 101 kPa, specific size of Al anodes with and without PTFE SMI

were placed in the headspace bottles containing 12 mL 0.1 M KOH electrolyte for 60 min respectively. The system was placed in a water tank to maintain the temperature of 25 °C. The mass of the system was weighed every 5 min (Δt_H) using an electronic balance (index value of 0.1 mg), and the weight loss Δm_n (mg) was considered the mass of hydrogen. The cumulative amount of hydrogen evolution $\sum m_n$ (mg) was calculated as Eq. (1). The corrosion rate v_n (mg cm⁻²min⁻¹) and anticorrosion efficiency η (%) were calculated as Eq. (2) and (3), respectively.

$$\sum m_n = \Delta m_1 + \dots + \Delta m_n \quad (1)$$

$$v_n = \frac{\Delta m_n}{S \cdot \Delta t_H} \quad (2)$$

$$\eta = \frac{\bar{v}_{Al} - \bar{v}_{PTFE}}{\bar{v}_{Al}} \cdot 100\% \quad (3)$$

where S is the surface area of the anode sample, which is 2.24 cm² in this test. \bar{v}_{Al} and \bar{v}_{PTFE} are the average corrosion rates of Al anodes without and with PTFE SMI, respectively.

Electrochemical measurement

Electrochemical measurement was performed with a three-electrode system using CHI660E electrochemical workstation, which anode (1×1 cm) as the working electrode, Hg/HgO (1 M KOH) as the reference electrode, and Pt plate (15×15 mm) as the counter electrode. In the 0.1 M KOH electrolyte, the Al anodes with and without PTFE SMI were shelved for 300 s to achieve interface stability. After that, the Tafel curve was tested based on a voltage range of -2.0~-0.5 V and a scanning rate of 5 mV s⁻¹. And then, electrochemical impedance spectroscopy (EIS) was recorded based on the frequency range of 0.1-100 kHz and AC amplitude of 5 mV s⁻¹, and then the Nyquist diagram and Bode plot were obtained. Finally, the linear sweep voltammetry (LSV) curve of the battery was tested based on the steady state open circuit potential with a scan rate of 0.05 V s⁻¹.

Materials characterization

For prepared Al anodes with and without PTFE SMI, Scanning Electron Microscopy (SEM) was obtained using a Thermofisher Teneo FE-SEM, and Water Contact Angle was also tested using Kruss EasyDrop Drop Shape Analyzer. For different Al anodes after the battery discharge, Raman

spectrum was acquired with a Renishaw inVia Raman microscope using a greenlight of 532 nm⁻¹ as wavelength, and X-ray diffraction (XRD) spectrum was tested with a Bruker D8 Advance system using Cu K α ($\lambda = 1.54 \text{ \AA}$) radiation. Besides, SEM images were also obtained.

Density functional theory (DFT) calculation

Interactions between Al (1 1 1) and PTFE (n=3)/H₂O molecules were analyzed based on DFT calculation. Firstly, the molecular models were constructed and optimized, thus the electrostatic potential and Mulliken charge were calculated. Subsequently, a 4 \times 4 Al (1 1 1) supercell with a vacuum layer thickness of 20 \AA was established. Consequently, the energy information of the interactions between Al (1 1 1) and PTFE (n=3)/H₂O molecules was ultimately calculated.

Performance evaluation of aqueous Al-air battery

Discharge performance of aqueous Al-air batteries using Al anodes with and without PTFE SMI was evaluated using NEWARE 7.5X battery testing system. Firstly, the voltage-current characteristic curve of the battery at 0, 1, 1.5, 2, 2.5 and 3 mA cm⁻² were recorded, and the duration of each current density was 5 min. Then, the battery duration ($\Delta t_{\text{battery}}$) at a current density of $I = 1 \text{ mA cm}^{-2}$ was tested, and the battery capacity Q (mAh g⁻¹) was thus calculated as Eq. (4). Finally, the cycling duration under the condition of 5 min-on (1 mA cm⁻²) and 5 min-off (0 mA cm⁻²) was tested to simulate the actual operation of the battery.

$$Q = \frac{I \cdot \Delta t_{\text{battery}}}{\Delta m_{\text{Al}}} \quad (4)$$

where Δm_{Al} (g) was the consumed mass of anode.

Supplemental figures:

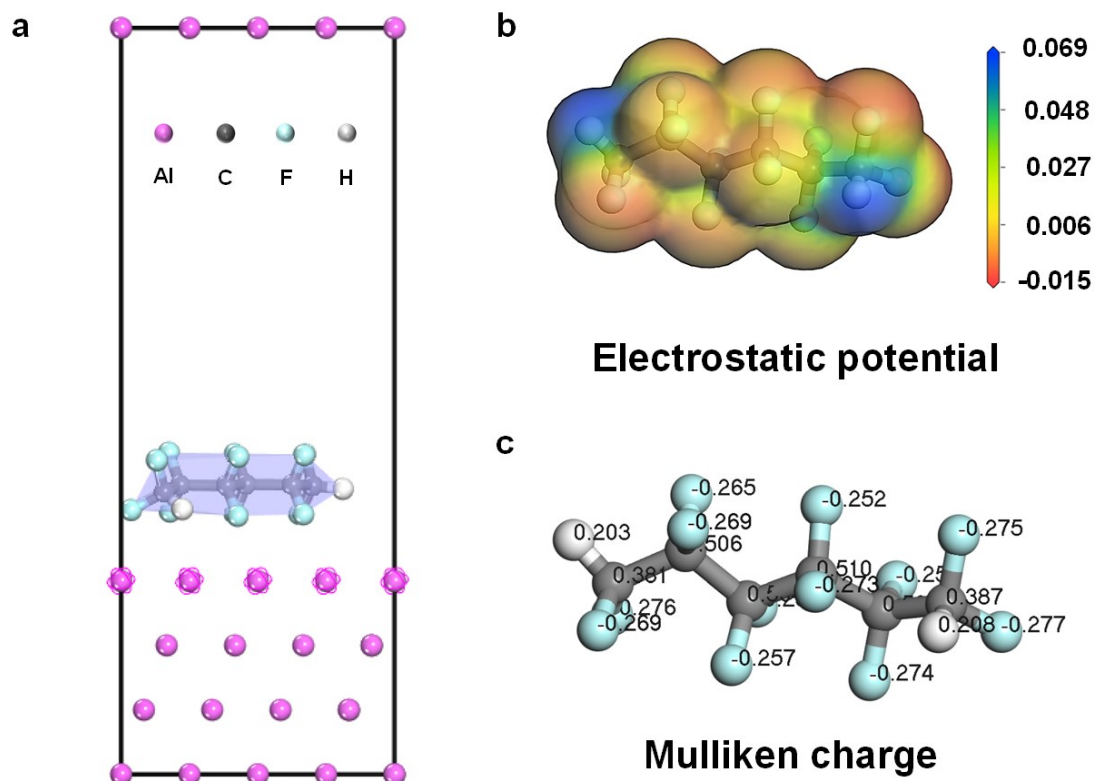


Fig. S1 DFT calculation: (a) Molecular model of Al (1 1 1) interacting with PTFE molecule ($n = 3$). (b) Electrostatic potential and (c) Mulliken charge of PTFE molecule ($n = 3$).

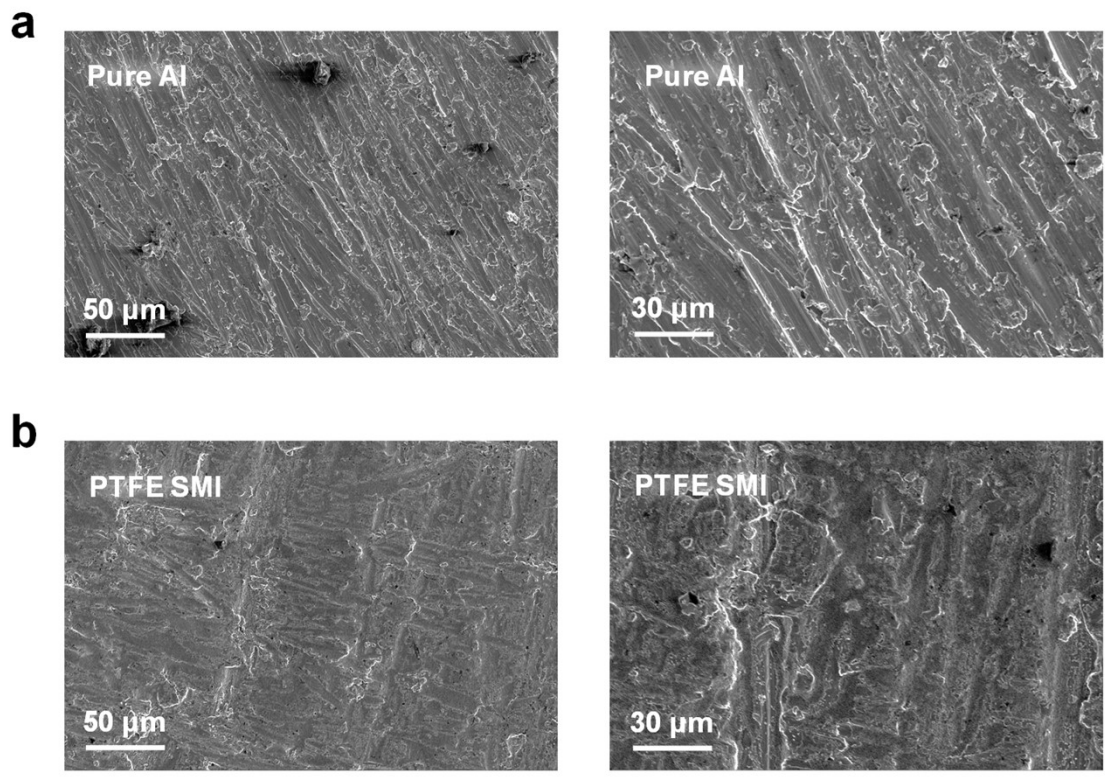


Fig. S2 Surface micromorphology of (a) prepared pure Al anode, and (b) prepared Al anode with PTFE SMI.

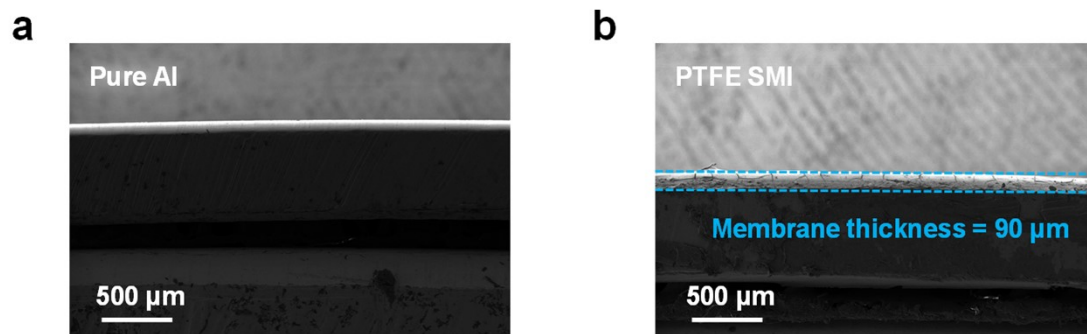


Fig. S3 Cross section micromorphology of (a) prepared pure Al anode, and (b) prepared Al anode with PTFE SMI.

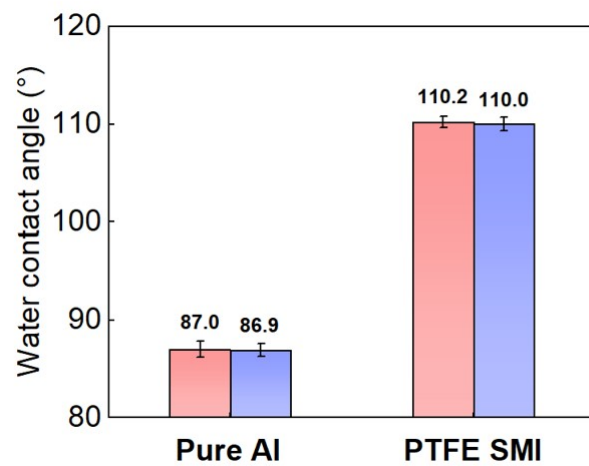


Fig. S4 The average value and error bar of the water contact angle for prepared Al anodes with and without PTFE SMI.

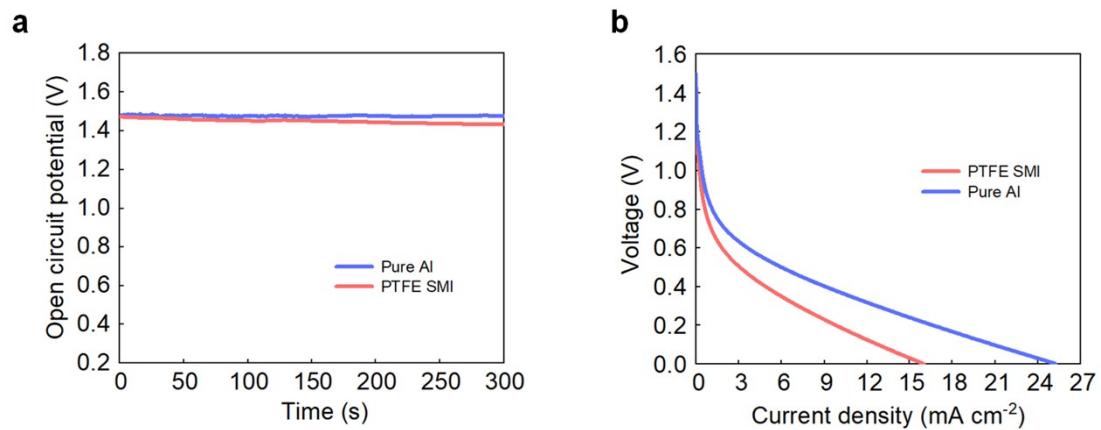


Fig. S5 (a) Steady state open circuit potential and (b) LSV curve of aqueous Al-air batteries using Al anodes with and without PTFE SMI.

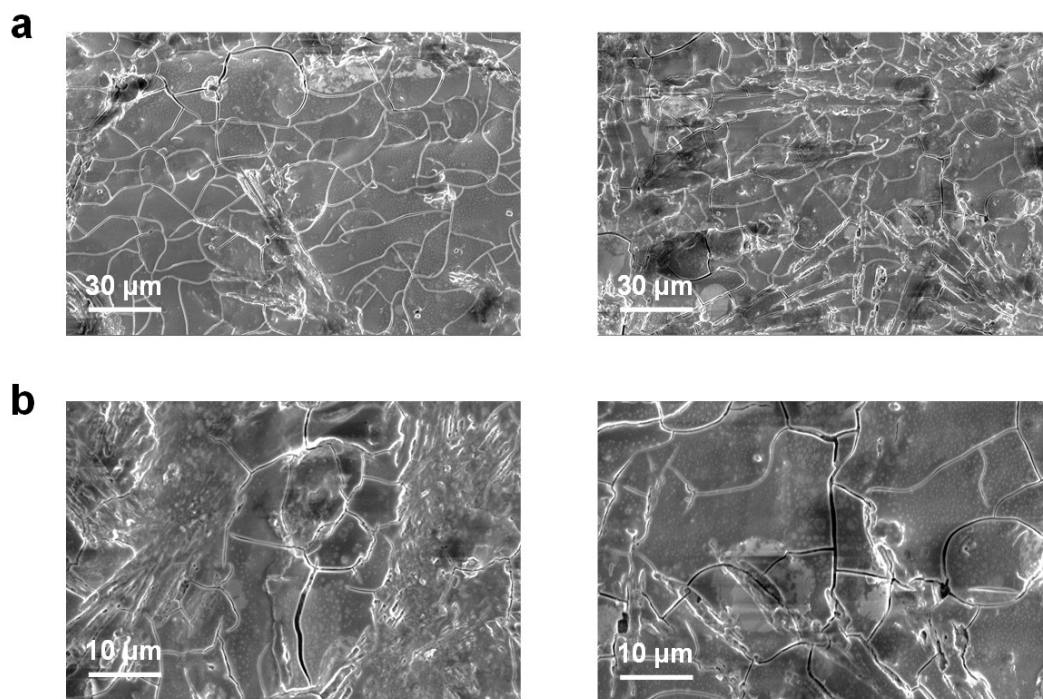


Fig. S6 Surface micromorphology of Al anode with PTFE SMI after battery discharge in scale of (a) 30 μm and (b) 10 μm.

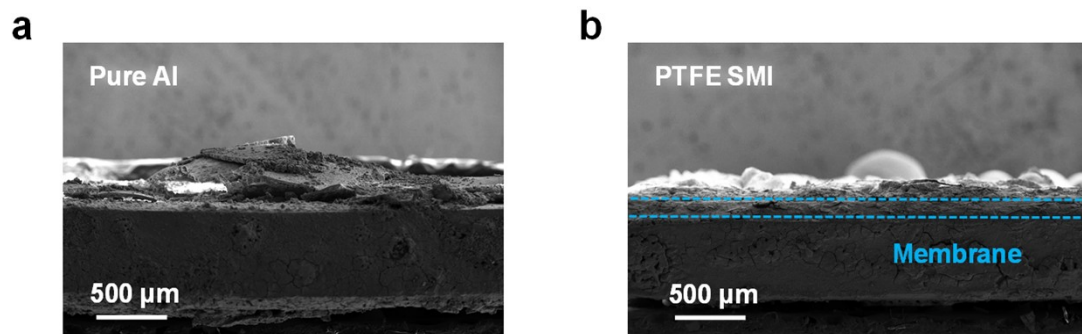


Fig. S7 Cross section micromorphology of (a) pure Al anode and (b) Al anode with PTFE SMI after battery discharge.

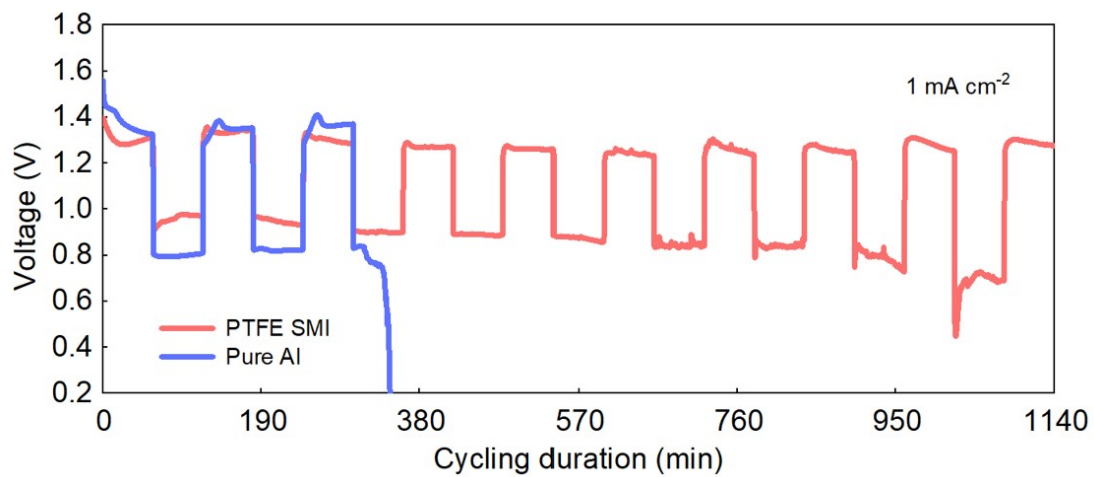


Fig. S8 Cyclic discharge lifetime of aqueous Al-air batteries using Al anodes with and without PTFE SMI under the condition of 60 min-on and 60 min-off.

Supplemental tables:

Table S1 Energy information of Al (1 1 1) interacting with different molecules involved in the current study.

Molecules	Binding energy (kcal/mol)
H ₂ O	-3.53
PTFE	-34.66

Table S2 Detailed Tafel parameters of different anodes immersion in 0.1 M KOH electrolyte.

Cases	E_{corr} (V)	i_{corr} (mA·cm ⁻²)	k_{c} (V·dec ⁻¹)	k_{a} (V·dec ⁻¹)
Pure Al	-1.312	1.739	5.612	4.218
PTFE SMI	-1.045	0.643	4.873	4.014

Table S3 Fitting EIS parameters of different anodes immersion in 0.1 M KOH electrolyte.

Cases	R_s (Ωcm^2)	CPE_1		R_{ct1} (Ωcm^2)	L (Hcm ²)	CPE_2		R_{ct2} (Ωcm^2)
		CPE_{1T}	CPE_{1P}			CPE_{2T}	CPE_{2P}	
		($\mu\text{Ss}^n\text{cm}^{-2}$)				($\text{mSs}^n\text{cm}^{-2}$)		
Pure Al	12.92	0.20	0.82	4.36	0.57	0.02	1.13	6.85
PTFE SMI	12.23	0.28	0.80	9.19	-	0.01	0.23	6.32

Table S4 Fitting EIS errors of different anodes immersion in 0.1 M KOH electrolyte.

Cases	R_s (%)	CPE_1		R_{ct1} (%)	L (%)	CPE_2		R_{ct2} (%)	χ^2 ($\times 10^{-3}$)
		CPE_{1T}	CPE_{1P}			CPE_{2T}	CPE_{2P}		
		(%)	(%)			(%)	(%)		
Pure Al	0.74	14.32	3.77	3.18	11.32	16.33	11.21	10.22	1.66
PTFE SMI	2.75	14.41	3.20	4.08	-	4.29	4.32	4.36	1.37